

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF STYRENE COPOLYMER RESIN FOAM

(57)Abstract:

PURPOSE: To obtain a molded foam with a good appearance and a controlled mean cell size by impregnating a specific copolymer with carbon dioxide as the blowing agent while adjusting the amt. of carbon dioxide dissolved.

CONSTITUTION: 98–75wt.% styrenic monomer such as styrene or α-methylstyrene and 2–25wt.% compd. having –OCO– group such as an acid anhydride e.g. maleic anhydride or methacrylic acid (maleic anhydride is pref.) are copolymerized to give a copolymer. After talc, a preventive against blocking during foaming, is attached to the copolymer, the copolymer is impregnated with carbon dioxide in an impregnation vessel while adjusting the pressure of carbon dioxide to 10–30kg/cm²G to adjust the cell sizes to 0.02–0.48mm and the mean cell size to 0.01–0.50 mm and then foamed with a pressurized steam. The resulting foamed particles are molded to give a molded foam.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacturing method of the fizz styrene system copolymer-resin mold goods which have the relation which the diameter of average air bubbles characterized by adjusting and infiltrating the amount of carbon dioxide gas as a foaming agent into the copolymer which contains a styrene system monomer and the compound which has a -OCO-radical as a polymerization component, and making it carry out foaming to the appropriate back becomes $0.01\text{mm} \leq (\text{diameter of average air bubbles}) \leq 0.50\text{mm}$.

[Claim 2] The manufacture approach of the styrene system copolymer-resin foam characterized by the compound which has a -OCO-radical according to claim 1 being a maleic anhydride.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the manufacture approach of styrene system copolymer-resin foam.

[Description of the Prior Art] Conventionally, the fizz styrene system copolymer particle which made the styrene system copolymer particle contain foaming agents, such as a propane, a pentane, and a methyl chloride, is well-known. Although it will become the pre-expansion particle which has many small air bubbles in it if this fizz styrene system copolymer particle is heated more than softening temperature It is filled up with these pre-expansion particle into the metal mold of the enclosed type which many stomata drilled in the wall surface. If heating media, such as a steam, are injected from the stoma, are heated more than the softening temperature of these particles and each particle is made to foam further, it will weld mutually and will become the Plastic solid of porous styrene system copolymerization of the same configuration as metal mold. The magnitude of the diameter of air bubbles in the porous styrene system copolymerization Plastic solid acquired by this approach has big effect on the physical properties and appearance of the foaming object. Therefore, the approach a cellular regulator adjusts the diameter of air bubbles, and the approach resin denaturation adjusts the diameter of air bubbles are proposed conventionally (JP,57-34296,B, JP,58-48575,B).

[0002] However, when a cellular regulator adjusts the diameter of air bubbles, it is necessary to change the class by the case where it enlarges with the case where the diameter of air bubbles is made small. Moreover, in order to act on the effect of the dispersibility inside [of a cellular regulator] resin, conditions until it results in foaming, and other additives etc. greatly, it was difficult to be stabilized continuously and to acquire the foaming object which has the diameter of air bubbles of arbitration.

[0003] On the other hand, when foam was obtained as an approach by resin denaturation, using a styrene maleic anhydride copolymer as resin, since organic blowing agents, such as butane, were conventionally used as foam, the diameter of air bubbles was the minimum, the shaping temperature range in the case of shaping became narrow, and that with which satisfaction goes enough also in physical properties was not obtained.

[0004] the copolymer with which this artificer etc. contains wholeheartedly the compound which has a styrene system monomer and a -OCO-radical as a polymerization component as a result of research — to a styrene maleic anhydride copolymer preferably By changing the amount of sinking in of the carbon dioxide gas to this resin at the time of foaming, using carbon dioxide gas as a foaming agent the diameter of average air bubbles of the foam obtained — changing — between both — **(diameter of average air bubbles of foaming object)1/(the amount of carbon-dioxide-gas sinking in to the resin at the time of foaming) — it finds out that relational expression is materialized and this invention is reached.

[0005]

[Means for Solving the Problem] This invention a styrene system monomer and the compound which has a -OCO-radical to namely, the copolymer included as a polymerization component It is the manufacturing method of the fizz styrene system copolymer-resin mold goods which have

the relation which the diameter of average air bubbles characterized by adjusting the amount of carbon dioxide gas as a foaming agent, infiltrating it, and carrying out foaming to the appropriate back becomes $0.01\text{mm} \leq (\text{diameter of average air bubbles}) \leq 0.50\text{mm}$. It is characterized by the compound which has a $-\text{OCO}-$ radical preferably being a maleic anhydride.

[0006] In this invention, styrene, alpha methyl styrene, vinyltoluene, KURORU styrene, etc. are mentioned as a styrene system monomer.

[0007] As a compound which has the $-\text{OCO}-$ radical which carries out copolymerization to a styrene system monomer, acid anhydrides, such as a maleic anhydride, a methacrylic acid, etc. are mentioned, and a maleic anhydride is mentioned preferably.

[0008] The compound which has a $-\text{OCO}-$ radical occupies 2 thru/or 25 % of the weight, and the rate of copolymerization in a copolymer is the thing of a rate [as / the complementary of whose is a styrene system monomer]. It is not said that that rate says the average and each copolymer molecules of all are within the limits of this. Therefore, in the case of a styrene maleic anhydride copolymer, the copolymer said by this invention mixes two kinds of things from which the rate of copolymerization differs, and the anhydrous MARENİ acid also contains in the whole 2 thru/or polymer mixture which came to be contained 25% of the weight. Moreover, the copolymer of this invention is the mixture of a styrene maleic anhydride copolymer and the homopolymer of styrene, and the maleic anhydride also contains in it 2 thru/or polymer mixture which is contained 25% of the weight.

[0009] As a copolymer which contains the compound which has the styrene system monomer and $-\text{OCO}-$ radical which are used for this invention as a polymerization component, the styrene maleic anhydride copolymer currently sold by the trade name of die Larc 232 can be used from the U.S. and an AKO polymer company company. In order to sink carbon dioxide gas into the copolymer which contains the compound which has a styrene system monomer and a $-\text{OCO}-$ radical as a polymerization component, it is based on the well-known approach of pressing carbon dioxide gas fit in the particle of this copolymer etc., for example. Adjustment of the amount of sinking in is based on the sinking-in pressure of carbon dioxide gas.

[0010] Foaming used for this invention is based on a well-known approach. For example, after carrying out pre-expansion of the resin into which carbon dioxide gas was infiltrated with steam under pressure and ripening it, this resin is put into a making machine, it heats with steam under pressure, welding of the resin particle is carried out mutually, and it considers as a foaming object.

[0011] if the thing of arbitration is obtained for the magnitude of the diameter of average air bubbles by changing the amount of carbon dioxide gas to this resin at the time of foaming according to this invention, but it is difficult for the molding-temperature region at the time of fabricating to become extremely narrow as for a less than 0.01mm thing, and for the magnitude of the diameter of average air bubbles to obtain a good foaming float and it is 0.5mm or more — an appearance — a beautiful thing is not obtained.

[0012] The resin in connection with this invention may be made to contain well-known additives, such as fusion inhibitors, such as a pigment, a flame retarder, and talc.

[0013]

[Example] Next, an example explains this invention.

It performed sinking in at 20 degrees C for 4 hours, having put what installed talc 5.0g as a fusion inhibitor at the time of foaming to 2kg of styrene maleic anhydride copolymers currently sold by the trade name of die Larc 232 into the saturator of 5L, changing the pressure of carbon dioxide gas variously according to an example, pressing it fit, and holding the pressure from the one to example 10 U.S., and an AKO polymer company company. Subsequently, the pressure of saturator was released and the resin with which it sank in carbon dioxide gas was taken out, and immediately after pressure disconnection or after 5 minutes, steam under pressure was used and it foamed. Foaming conditions were changed according to the example. (After taking some resin with which it sank in carbon dioxide gas at this time to the beaker (***) which carried out weighing capacity beforehand and measuring the weight 5 minutes after after pressure release (**), the amount of carbon-dioxide-gas sinking in to the resin at the time of foaming was calculated by the degree type by measuring the weight (***)) when leaving it in a thermostat for

90 degree-Cx 4 hours, and carrying out gradual cooling to a room temperature.)

Amount of carbon-dioxide-gas sinking in = $\frac{\text{[-- --]} - \text{[-- --]}}{\text{[-- --]}}$ to resin / 44×1000

Next, after ripening the obtained foaming grain at a room temperature, foam with good fabricating was obtained using the making machine which has the metal mold of L300xW400xH50. A result is shown in Table 1.

[Table 1]

	含浸圧力 (kg/cm ² G)	発泡時の炭酸 ガス含浸量 (wt%)	発泡条件 (°C × 秒)	発泡粒の 倍率 (倍率)	気泡径* (mm)	成形品の密度 (g/cc)
実施例1	10.2	2.3	134 × 45	24	0.43	0.040
実施例2			134 × 60	40	0.48	0.025
実施例3	14.6	2.7	132 × 30	23	0.34	0.045
実施例4			134 × 30	40	0.38	0.024
実施例5	20.5	3.8	128 × 30	24	0.18	0.041
実施例6			130 × 30	45	0.21	0.021
実施例7	24.8	4.3	125 × 45	23	0.08	0.043
実施例8			128 × 45	41	0.12	0.024
実施例9	29.5	4.6	125 × 30	22	0.02	0.046
実施例10			128 × 45	47	0.03	0.020

* 気泡径 = 測定値 / 0.616

(Note)

Measurement (diameter of average air bubbles) of the diameter of average air bubbles = 22 to 24 times as many ***** of an actual measurement / 0.616 process-condition foaming grain as this 2.3 (water vapor pressure) × 30 (second)

40 to 47 times 2.0 (water vapor pressure) × 30 (second)

[0014] In example of comparison 1~9 these examples of a comparison, the resin which blended polystyrene resin or polystyrene, and polyphenylene ether as resin was used. Foam was obtained like the example except it. A result is shown in Table 2.

[Table 2]

		含浸圧力 (kg/cm ² G)	発泡時の炭 酸ガス含浸 量 (wt %)	発泡条件 (°C×秒)	発泡粒の 倍率 (倍率)	気泡径 (mm)
比較例1	ポリ ス チ レ ン	7.5	1.9	133×30	53	0.062
比較例2		14.0	2.6	125×45	49	0.058
比較例3		21.0	4.3	121×45	50	0.070
比較例4		25.7	5.4	121×30	54	0.068
比較例5		30.5	6.2	118×30	51	0.065
比較例6	ポリ フ エ ニ チ レ ン / ポリ ス チ レ ン エ ー タル	10.5	1.8	141×60	23	0.045
比較例7		21.5	3.6	136×60	20	0.052
比較例8		29.0	5.6	133×60	24	0.048
比較例9		39.5	7.5	133×30	21	0.050

Relation fixed between the diameter of air bubbles of these foam and the amount of sinking in at the time of foaming was not seen.

[0015] 1.86 mols of butane were added to 1kg of resin as a foaming agent, the temperature up was carried out to 105 degrees C, adding and stirring the styrene 100 weight section, the water 100 weight section, the phosphoric acid tricalcium 0.15 weight section, and the sodium dodecylbenzenesulfonate 0.005 weight section in the proof-pressure reactor possessing example of comparison 10 agitator, and a temperature indicator tube, and it performed sinking in for 6 hours. After cooling this to a room temperature, the pre-expansion particle 42 times the ***** of this was obtained using the pressurization steam after ejection dehydration, and it fabricated like examples 1-10. The average air bubbles of the obtained mold goods were very dense things 0.01mm or less, and were that in which an appearance is also inferior compared with the mold goods of examples 1-10.

[0016] 0.92 mols of example of comparison 11 butane, 1kg of resin, and others 45 times the ***** of this were performed like the example 10 of a comparison. The appearance of the obtained mold goods was what is inferior compared with the mold goods of examples 1-10. In addition, change was not looked at by air bubbles even if it changed the amount of a foaming agent in the examples 10 and 11 of a comparison.

[0017]

[Effect of the Invention] Since carbon dioxide gas is used for the copolymer which contains the compound which has a styrene system monomer and a -OCO-radical as a polymerization component in this invention as a foaming agent The diameter of average air bubbles of the foam obtained by changing the amount of sinking in of the carbon dioxide gas to this resin at the time of foaming also changes. between both — **(diameter of average air bubbles of foaming object) 1/(the amount of carbon-dioxide-gas sinking in to the resin at the time of foaming) — the diameter of average air bubbles which relational expression is materialized, therefore is a good

foaming object — 0.01mm<=(diameter of average air bubbles) <=0.50mm — the foaming object which has a relation can be acquired easily.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacture approach of styrene system copolymer-resin foam.

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PRIOR ART

[Description of the Prior Art] Conventionally, the fizz styrene system copolymer particle which made the styrene system copolymer particle contain foaming agents, such as a propane, a pentane, and a methyl chloride, is well-known. Although it will become the pre-expansion particle which has many small air bubbles in it if this fizz styrene system copolymer particle is heated more than softening temperature It is filled up with these pre-expansion particle into the metal mold of the enclosed type which many stomata drilled in the wall surface. If heating media, such as a steam, are injected from the stoma, are heated more than the softening temperature of these particles and each particle is made to foam further, it will weld mutually and will become the Plastic solid of porous styrene system copolymerization of the same configuration as metal mold. The magnitude of the diameter of air bubbles in the porous styrene system copolymerization Plastic solid acquired by this approach has big effect on the physical properties and appearance of the foaming object. Therefore, the approach a cellular regulator adjusts the diameter of air bubbles, and the approach resin denaturation adjusts the diameter of air bubbles are proposed conventionally (JP,57-34296,B, JP,58-48575,B).

[0002] However, when a cellular regulator adjusts the diameter of air bubbles, it is necessary to change the class by the case where it enlarges with the case where the diameter of air bubbles is made small. Moreover, in order to act on the effect of the dispersibility inside [of a cellular regulator] resin, conditions until it results in foaming, and other additives etc. greatly, it was difficult to be stabilized continuously and to acquire the foaming object which has the diameter of air bubbles of arbitration.

[0003] On the other hand, when foam was obtained as an approach by resin denaturation, using a styrene maleic anhydride copolymer as resin, since organic blowing agents, such as butane, were conventionally used as foam, the diameter of air bubbles was the minimum, the shaping temperature range in the case of shaping became narrow, and that with which satisfaction goes enough also in physical properties was not obtained.

[0004] the copolymer with which this artificer etc. contains wholeheartedly the compound which has a styrene system monomer and a -OCO-radical as a polymerization component as a result of research — to a styrene maleic anhydride copolymer preferably By changing the amount of sinking in of the carbon dioxide gas to this resin at the time of foaming, using carbon dioxide gas as a foaming agent the diameter of average air bubbles of the foam obtained — changing — between both — **(diameter of average air bubbles of foaming object)1/(the amount of carbon-dioxide-gas sinking in to the resin at the time of foaming) — it finds out that relational expression is materialized and this invention is reached.

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EFFECT OF THE INVENTION

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MEANS

[Means for Solving the Problem] This invention a styrene system monomer and the compound which has a -OCO-radical to namely, the copolymer included as a polymerization component It is the manufacturing method of the fizz styrene system copolymer=resin mold goods which have the relation which the diameter of average air bubbles characterized by adjusting the amount of carbon dioxide gas as a foaming agent, infiltrating it, and carrying out foaming to the appropriate back becomes $0.01\text{mm} \leq (\text{diameter of average air bubbles}) \leq 0.50\text{mm}$. It is characterized by the compound which has a -OCO-radical preferably being a maleic anhydride.

[0006] In this invention, styrene, alpha methyl styrene, vinyltoluene, KURORU styrene, etc. are mentioned as a styrene system monomer.

[0007] As a compound which has the -OCO-radical which carries out copolymerization to a styrene system monomer, acid anhydrides, such as a maleic anhydride, a methacrylic acid, etc. are mentioned, and a maleic anhydride is mentioned preferably.

[0008] The compound which has a -OCO-radical occupies 2 thru/or 25 % of the weight, and the rate of copolymerization in a copolymer is the thing of a rate [as / the complementary of whose is a styrene system monomer]. It is not said that that rate says the average and each copolymer molecules of all are within the limits of this. Therefore, in the case of a styrene maleic anhydride copolymer, the copolymer said by this invention mixes two kinds of things from which the rate of copolymerization differs, and the anhydrous MAREN1 acid also contains in the whole 2 thru/or polymer mixture which came to be contained 25% of the weight. Moreover, the copolymer of this invention is the mixture of a styrene maleic anhydride copolymer and the homopolymer of styrene, and the maleic anhydride also contains in it 2 thru/or polymer mixture which is contained 25% of the weight.

[0009] As a copolymer which contains the compound which has the styrene system monomer and -OCO-radical which are used for this invention as a polymerization component, the styrene maleic anhydride copolymer currently sold by the trade name of die Larc 232 can be used from the U.S. and an AKO polymer company company. In order to sink carbon dioxide gas into the copolymer which contains the compound which has a styrene system monomer and a -OCO-radical as a polymerization component, it is based on the well-known approach of pressing carbon dioxide gas fit in the particle of this copolymer etc., for example. Adjustment of the amount of sinking in is based on the sinking-in pressure of carbon dioxide gas.

[0010] Foaming used for this invention is based on a well-known approach. For example, after carrying out pre-expansion of the resin into which carbon dioxide gas was infiltrated with steam under pressure and ripening it, this resin is put into a making machine, it heats with steam under pressure, welding of the resin particle is carried out mutually, and it considers as a foaming object.

[0011] if the thing of arbitration is obtained for the magnitude of the diameter of average air bubbles by changing the amount of carbon dioxide gas to this resin at the time of foaming according to this invention, but it is difficult for the molding-temperature region at the time of fabricating to become extremely narrow as for a less than 0.01mm thing, and for the magnitude of the diameter of average air bubbles to obtain a good foaming float and it is 0.5mm or more — an appearance — a beautiful thing is not obtained.

[0012] The resin in connection with this invention may be made to contain well-known additives, such as fusion inhibitors, such as a pigment, a flame retarder, and talc.

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EXAMPLE

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Amount of carbon-dioxide-gas sinking in ={**-**}/{**-**} to resin / 44x1000

Next, after ripening the obtained foaming grain at a room temperature, foam with good fabricating was obtained using the making machine which has the metal mold of L300xW400xH50. A result is shown in Table 1.

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[0014] In example of comparison 1~9 these examples of a comparison, the resin which blended polystyrene resin or polystyrene, and polyphenylene ether as resin was used. Foam was obtained like the example except it. A result is shown in Table 2.

[Table 2]

		含浸圧力 (kg/cm ² G)	発泡時の炭 酸ガス含浸 量 (wt %)	発泡条件 (°C × 秒)	発泡粒の 倍率	気泡径 (mm)
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比較例6	ポリ フエ ニレ ン/ ポリ スチ レン エーテ ル	10.5	1.8	141 × 60	23	0.045
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